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Development of an Easily Deinkable Copy Toner Using Soy-based Copolyamides

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Abstract

To develop an easily deinkable toner for office copiers and laser printers, a series of homo- and copolyamide toner resins were synthesized via condensation polymerization of soy-based dimer acid, 1,4-phenylenediamine, and L-tyrosine (an α-amino acid). The thermal properties of the resins were examined using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). It was found that the glass transition temperature (T_g), melting point (T_m), decomposition temperature (T_d) and crystallinity of the copolyamides were remarkably decreased as the content of L-tyrosine was increased. By using both homo- and copolyamides as binders, respectively, two dual-component toners were developed. The triboelectrical charge, particle size and particle size distribution of these toners were examined. The printing trials demonstrated that the images of the soy-based toners are similar to that of commercially available toners. However, because of the low crystallinity and high water-uptake ability of the amino acid-containing polyamide, the copolymer is swellable in an alkaline solution. Initial results from flotation deinking suggest that the amino acid-containing toners are more easily deinked likely due to their high swellability.

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Introduction

Waste paper recycling is of growing importance, both for better utilization of the natural resources of wood, and for reduction of the amount of solid waste. Legislation requiring specific percentages of recycled fiber in paper products is forcing paper manufacturers to utilize waste streams that were previously sent to landfills. However, it has been found that office waste paper printed with a polymer-based toner is one of the most difficult paper grades to deink [1,2]. Although many new techniques [3-5] have been developed for deinking electrostatically-printed papers, the relative high cost and low deinking efficiency are still problems to be resolved. Therefore, a toner resin that can be easily deinked is desirable for paper recycling.

Different petroleum-based polymers, such as polystyrene, polyester, polyamide, polyethylene, poly(ethylene-co-vinyl acetate) and poly(styrene-co-butyl methacrylate), have been widely used as toner binders [6-10]. In order to develop a high performing toner, the polymer binder must have suitable molecular weight, glass transition temperature (T_g), melting viscosity, and electrical properties [11]. The common toners have a T_g ranging from 50 to 65°C, and a fusing temperature of approximately 60 to 120°C above their T_g. Toner's melt viscosity is dependent on various parameters such as copolymer ratio, molecular weight, and branching and crosslinking, and can directly impact the xerographic performance. Although many different petroleum-based polymers have been used as toner binders, little work has been done to use a natural product as a raw material for toner production. Compared tocurrently used petroleum-based toner resins, soy-based resins possess some advantages. The materials are renewable, nontoxic, of potentially lower cost, and provide strong adhesion to most paper surfaces. In this study, soy-based dimer acids were chosen as a raw material for preparation of toner resins.

In a typical xerographic process, the toner particles are melted and fused into the paper matrix at high temperature and pressure. Because the toner resin strongly anchors with fibers during cooling, it is difficult to remove the toner particles from fibers [12], resulting in poor fiber-ink separation and low deinking efficiency of the wastepapers. In order to improve deinking efficiency of toner printed paper, one of the possible methods is to produce a swellable toner. Therefore, it might be easier to remove the toner particles from the wood fiber surface due to the swelling of the toner particles, which might reduce the bonding strength between toner and fibers during repulping of the wastepaper.

Recently, Arvanitoyannis et al. [13-15] have prepared a series of amino acid-containing polyamides. They reported that these polyamides are biodegradable. Because amino acids contain both amine and acid groups, incorporation of amino acid into a polymer backbone may significantly impact the polymer structure, the crystallinity, and the swellability. Although the incorporation of amino acids into polyamides has been reported [13-15], the copolymerization and the characterization of an amino acid with soy-based polyamides have not been reported in the literature. In this study, soy-based polyamides with and without an α-amino acid (L-tyrosine) were synthesized. The thermal and swelling behavior of both homo- and co-polyamides were examined. The compounding and processing of a dual component toner using these polyamides as binders were explored. The printing and flotation deinking trials were also carried out using toners produced in our laboratories.

Experimental**Materials:** The dimer acid used in the synthesis was supplied by the Emery Group of Henkel Corporation (Cincinnati, OH). Empol 1016 dimer acid is a yellowish viscous liquid at room temperature with the ratio of dimer totrimer to monomer at 97:2:1, L-tyrosine (l-3-[4-Hydroxyphenyl]-alanine) was obtained from Sigma (St. Louis, MO), and 1,4-phenylenediamine was purchased from Aldrich (Milwaukee, WI). Both were used as received without further purification. Their acronyms, reported purity, molecular structure and melting points are listed in **Table 1.**

Polymer and copolymer synthesis: Copolymers were synthesized by condensation polymerization. A typical example of polymerization for a copolymer with 12.7 wt% tyrosine (based on total weight of starting monomers) is described here. Amount of 50 g of dimer acid (equivalent to 0.174 mol of acid groups) was charged into a 250-ml three-necked round bottom flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet. The monomer was first heated to 80°C under a nitrogen atmosphere and vigorous stirred, then 9.6 g of 1,4-phenylenediamine (equivalent to the total acid groups) and 8.7 g of L-tyrosine were added. The reactants were gradually heated to 250°C over 3 hours and kept at this temperature for another 5 hours being stirred vigorous, then the system was allowed to cool down to room temperature. The next day the reactants were heated again to 250°C and subjected to a vacuum of approximately 2 mm Hg for 4 hours. The product was then discharged from the flask.

DSC and TGA analysis: DSC measurements were performed on a SEICO DSC equipped with a thermal analysis station. TGA measurements were carried out on a SEICO TGA. Both DSC and TGA measurements were performed under nitrogen at 20°C/min and 10°C/min heating rate, respectively.

Swelling test: Water uptake of the samples was determined at different pH values at 70°C to study the polymer's swelling behavior. Dry polymer film samples with a fixed surface area and thickness (15 mm × 10 mm × 0.05 mm) were carefully weighed and put into a test tube, then 15 ml water at the required pH was added. The test tube was put into an isothermal bath at a fixed temperature for 24 hours. The sample was then taken out and washed with distilled water. Before weighing the sample, the film surface was carefully wiped with a paper towel to remove free water. The water uptake was then calculated as the weight difference before and after water immersion.

Toner production: A homopolyamide (D-P) and a copolyamide (D-P-T) made by adding 7.7 wt% of L-tyrosine to the monomers were used in the toner production. The resin was first blended with carbon black as the pigment (Regal 330, CABOT Corporation), and a charge controlling agent (Copy Blue PR, Hoechst High Chem Pigment) in a Two Roll Mill at 80°C for 30 minutes. A homogeneous dispersion of pigment in the polymer was observed. The polymer was then ground to the required particle size of about 10 μm, using an Air-Jet Mill (Toner Research Services) at a feed rate of 3 g/min and air pressure of 100 psi. After pulverization, the dry toner was subjected to classification to remove particles less than 5 and greater than 15 μm using a CCE Model 100 Classfier.

Toner characterization: A multi-channel particle counter, Model PCA II (Coulter Electronics Inc.), was employed to measure the particle size and particle size distribution. Isoton III solution was used as the media for circulating the particles through the detector. In an effort to minimize coagulation, 10 ml of soap solution (2g/liter) was added to the system before measuring. The triboelectric charge value of the toner with a carrier (Type 29 Carrier Power, Vertex Image Products Inc.) was measured using the blow-off technique with an apparatus built at the Georgia Institute of Technology. This technique measures the charge per mass of the developer in microcoloumbs/gram.

Flotation deinking: The pulp suspension used for the flotation deinking was made from bond paper printed using the two soy-based toners with a fixed pattern of letter X to control amount of toner deposited. The papers were pulped at pH of 7.0 and 10.8, respectively, with a consistency of 10.5% without adding other chemicals. Flotation deinking was carried out using a laboratory flotation cell. The deinking cell was made from a polyacrylate pipe with a height of 80 cm and a diameter of 10 cm. Nitrogen gas was blown into the pulp suspension at a rate of 14±0.075 SLPM (standard liters per minute) through an air filter (pore size 50 μm) at the bottom of the flotation cell for all experiments. The flotation time was 10 minutes. The air flowrate was measured with an Omega FMA 1700/1800 flowmeter. The consistency of the pulp used in flotation was 0.5%. A nonionic surfactant, TX-100, was used as frothing agent.

Brightness measurement: The handsheets for the brightness analysis (deinking efficiency) of deinked pulp were made on a 15-cm Büchner funnel according to TAPPI Standard Method T218 om-91. The brightness of a handsheet was measured using a UV-

VIS spectrophotometer (Shimadzu UV-160A) using TAPPI Standard Method T452 om-92.

Results and Discussion

Physical properties of homo- and copolyamides: Synthesis of polyamides using a dimer acid and a diamine is a typical condensation polymerization, which usually takes place through the elimination of water molecules at certain reaction conditions. The molecular weight of dimer acid-based polyamides can be affected by reaction time, temperature, monomer ratio, catalyst, etc. If other parameters remain constant, the reaction temperature, which is directly related to the rate of distillation of the condensing water, will significantly affect both the polymerization rate and the molecular weight. The reaction conditions as well as their effect on the homopolyamide's physical properties were given in a previous publication [16]. The acronyms and molecular structures of soy-based polyamides that were used here for toner production and printing are given in **Table 2**. The DCS and TGA measurements indicate that this soy-based polyamide has a glass transition temperature of 68°C, a melting temperature of 127°C, and a decomposition temperature of 397°C. These values suggest that it is a suitable candidate for a toner resin [11].

It is well known that incorporation of α-amino acids, such as glutamic acid and lysine, in polymers can produce functional polymers and enhance the polymer's water sensitivity and biodegradability [13-15]. In order to modify the soy-based polyamide's swelling and biodegradation properties, and to thereby create an easily deinkable toner, a series of soy-based copolyamide resins was synthesized by incorporating different amount of L-tyrosine into the homopolymer. Because amino acid has both amine and acid groups, it can be easily copolymerized with dimer acid and diamine at a high temperature. The thermal properties of copolyamides with different weight percentages of tyrosine are shown in **Figure 1** and **Table 3**. Evidently, by increasing the content of tyrosine, the copolymer's glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH), and decomposition temperature (T_d) are gradually decreased. The results suggest that tyrosine can copolymerize with soybean dimer acid and phenylenediamine. The incorporation of tyrosine segments into the dimer acid-phenylenediamine (D-P) matrix may interrupt the original regular chain structure of D-P. As a result, the crystallinity decreased, which led to lower T_g, T_m, ΔH and T_d. Interestingly, when the tyrosine content increased to over 20 wt%, the copolymer's melting peak completely disappeared (**Figure 1**), and both T_g and T_d shifted to lower temperatures. The result may imply that when over 20 wt% of tyrosine was incorporated, the crystallization process in the copolymer could be greatly inhibited by introducing a large number of heterogeneous segments [17]. Unfortunately, the T_g of the copolymer with 20 wt% of tyrosine is too low, resulting in a soft and tacky polymer at room temperature. Therefore, it cannot be used as a toner resin [11].

Swelling behavior of homo- and copolyamides: One of the methods to produce an easily deinkable toner for copiers may be to use a water swellable polymer binder in the toner formulation. The swelling properties of the polymer samples in aqueous solution measured over a wide range of pH values are shown in **Figure 2**. Evidently, the values of water uptake of D-P homo-polymer is almost unchanged from pH 2 to 12 at 70°C for 24 hours. The poor swelling properties of the homopolyamide may be closely related to the molecular chain structure and crystallinity. From **Table 1** it can be seen that the soybean dimer acid contains a cyclic structure with several long flexible aliphatic branches. Compared to phenylenediamine, the structure of soybean dimer acids is more complicated. The average molecular weight of soybean dimer acid is about 570, which is much larger than that of phenylenediamine (108). When both monomers react stoichiometrically to form a polymer, the mass ratio of amide in the polymer should be relatively low. Thus, the characteristics of the molecular chain structure of the homopolyamide could be considered as containing mostly hydrophobic segments with a small amount of amide linkages, which possess certain hydrophilic properties. On the other hand, in our previous study [16] it was demonstrated that soy-based aromatic polyamides (D-P) are typical semicrystalline polymers with a relatively high crystallinity, better mechanical performance, and excellent thermal stability. As a result, its chain character and physical properties could effectively resist the penetration of water molecules into its amorphous matrix even in a strong alkaline, or acid solution, or a relatively hightemperature enviroment.

However, compared to the homopolyamide, the swellability of copolyamides is improved remarkably by increasing the content of amino acid. As can be seen from **Figure 2**, the increase in swellability of copolymers is a function of the amount of amino acid incorporated, i.e., the more amino acid in copolymer, the more water uptake can be obtained. The results may be attributed to the enlarged amorphous phase due to the lowered crystallinity of copolyamides (**Figure 1**), and the presence of more hydrophilic functional groups of amino acid in the polymer matrix. **Figure 2** also shows that, for the sample containing 16.8% D-P-T, there is a great increase in the amount of water uptake at pH 12 and 70°C. The result may imply that higher levels of amino content in copolymers could lead to easier attack by strong alkaline solutions, resulting in enhanced swelling.

Toner production and testing: Two dual component toners produced from D-P and D-P-T (7.7%) are listed in **Table 4**. The physical properties of the toners indicate that both D-P and D-P-T (7.7%) can be successfully compounded and ground into the required particle size, i.e., an average particle size around 10 μm and a particle size distribution around 90% > 5 microns. Compared with the Colorocs Company's toner, soy-based polyamide toners have the potential to achieve a similar print quality to that produced by commercial toners. It should be noted that the particle size and its distribution are two critical properties that can greatly affect resolution, imaging, and printing background during copying. Usually, larger particles decrease the resolution of the image, and smaller particles may result in smearing of the image, increasing the gray background, and even damaging the print. In general, the toner particle size required for a commercial toner is around 10 μm [11].

The particle size and particle size distribution depend on many factors, such as T_g of polymer binders, and the processing conditions during production. As mentioned previously, the polymer's T_g is quite important for producing a high performance toner. If T_g is too low, it is difficult to grind an amorphous polymer to the required particle size because the polymer particles are likely to stick together in the process. However, our results suggest that soy-based polyamides, both with and without aminoacid, can be easily compounded and ground to the required particle size using a standard air mill.

The triboelectric charge is another key parameter for toners. The triboelectric charge evaluates the electrical performance of a particular carrier-toner combination. Since a Colorocs Color Paper Copier (Model CP 4007) is used in our printing test, the commercial Colorocs black toner was used as a standard for comparison. Colorocs black toner has a triboelectric charge of 10.0 microcoulomb/gram (μc/g). Compared to the values of 12.6 and 15.5 μc/g of our soy-based toner (**Table 4**) made from D-P and D-P-T (7.7%), soy-based toners made in this srudy have a closed triboelectric charge to that of Colorocs toner. The visual impression of the printing results indicated that the soy-based toners are capable of producing a high-quality image and is at least equivalent to the standard commercial toner.

Deinking tests: In customary deinking tests, printed sheets of paper are disintegrated into a pulp (repulping), and then deinked by flotation. Flotation takes advantage of the hydrophobic surface properties of polymeric toners, compared to the hydrophilic surfaces of wood fibers. The deinked pulp is then used to manually form sheets of paper (called handsheets) according to standardized methods.

The deinking efficiency of toner-printed paper was evaluated by measuring the brightness gain of the handsheets made from deinked pulps after flotation deinking. From **Figure 2** it is clear that the amino acid-containing polyamide can swell at elevated pH and temperature, but that the homopolyamide sorbs much less water. To examine the effect of toner swellability on the ink-fiber detachment, the repulping and deinking of waste papers printed using both toners was carried out at pH 11 and temperature of 60 °C. The flotation deinking results are shown in **Figure 3**. It can be seen that the brightness gain of handsheets from repulped and flotation deinked paper printed with D-P-T (7.7%) toner is consistently higher than that of handsheets produced from repulped and deinked D-P toner-printed paper. Further experiments indicate that the ink particles of amino acid-containing toner [D-P-T (7.7%)] are much smaller than those of homopolyamide toner. These results suggest that the amino acid-containing toner may be more easily separated from fiber surfaces and broken into small particles at a high pH and temperature during the repulping. However, it should be noted that flotation deinking efficiency depends on many factors, including the surface chemistry of toner particles, the foam stability and structure, the size of toner particles and air bubbles. Therefore, more work is needed to obtain a full understanding of the effect of toner particle swelling on the toner-fiber detachment during the repulping.

Conclusions

It has been demonstrated in this study that an amino acids, such as L-tyrosine, can be copolymerized into soy-based polyamide using a condensation polymerization technique. The copolymer's glass transition temperature (T_g), melting temperature (T_m), enthalpy of fusion (ΔH), and decomposition temperature (T_d) are gradually decreased as the content of tyrosine is increased. Compared to a homopolyamide, the swellability of copolyamides at elevated pH and 70°C increases with increasing content of amino acid in the polymer backbone.

Both soy-based homo- and copolyamides were compounded and processed into a dual component toners, which achieved the same printing performance as a commercial toner.

The performance of our toners in recycling of toner-printed paper (toner removal from repulped paper by flotation) was investigated. Flotation deinking results indicated that the toner with an amino-acid containing copolyamide can be more easily removed from the repulped paper slurry at elevated pH of the solution. It can be speculated that this is due to increased water sorption of the copolymer-based toner.

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Figure Captions

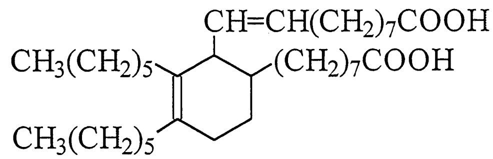
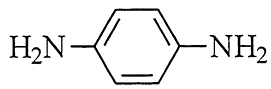
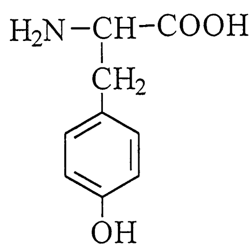
Figure 1. DSC diagrams for D-P and D-P-T with varying L-tyrosine content.

Figure 2. Water uptake percentage for D-P and D-P-T L-tyrosine content.

versus pH at 70°C for 24 hours.

Figure 3. Brightness of handsheets made by flotation deinked pulps as a function of surfactant concentration.

Table 1. Characteristics of the monomers

Monomer	Acronym	Structure	T_m/° C
Dimer acid*	D		Liquid at room temperature
1,4-Phenylene-diamine (99%)	P		143-145
L-tyrosine	T		135

*D: Dimer Acid (Empol 1016) contains 97% dimer, 2% trimer, and 1% monomer acids.

Table 2. Characteristics of the polymers

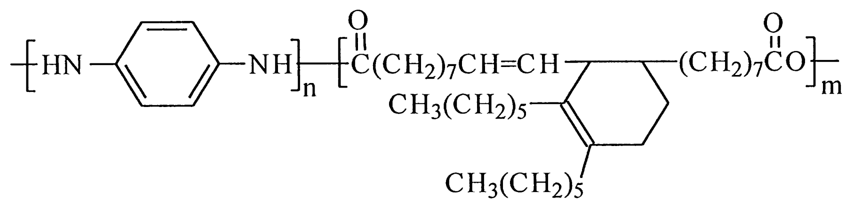
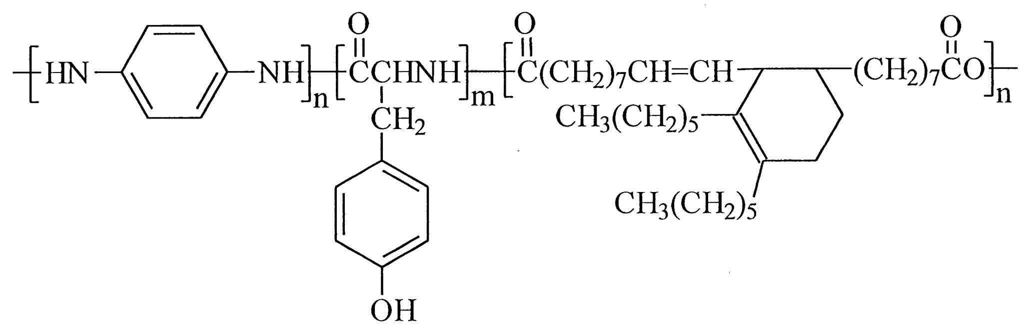
Copolymer	Structure
D-P (Homopolyamide of dimer acid and phenylenediamine)	
D-P-T (Based on dimer acid 1016, phenylenediamine and tyrosine)	

Table 3. Physical properties of soy-based polyamides

Copolymers with different weight percent of tyrosine (%)	Glass transition temperature (°C)	Melting temperature (°C)	Enthalpy of fusion (J/g)	Decomposition temperature (°C)
0.00	68	127	16.7	397
6.80	30	113	13.1	393
12.70	29	93	7.5	374
16.80	26	87	-	361
21.20	21	-	-	361

Table 4. Characteristics of the toners

Polymer	Particle size (Volume average) n_v (μm)	Particle size (Population average) n_p (μm)	Particle size distribution (Volume average)	Triboelectric charge* (μc/g)
Colorocs	10.4	-	98.64% > 5μm	8.5
D-P	11.5	9.0	90.71% > 5μm	12.6
D-P-T**	10.8	8.2	91.88% > 5μm	15.5

*: Vertex Image carries were used, and toner concentration is 6%.

**: L-tyrosine content in copolymer is 7.7%.

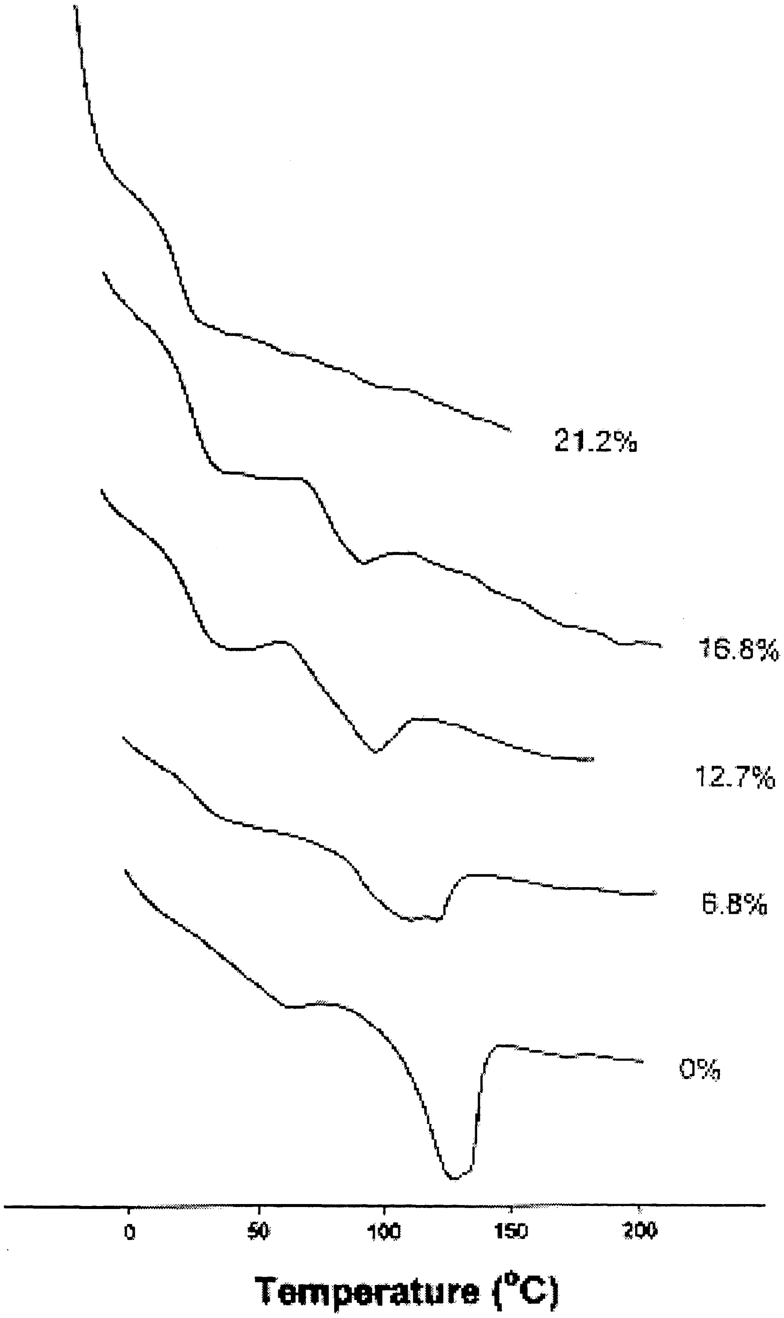


Figure 1. DSC diagrams for D-P and D-P-T with varying L-tyrosine content.

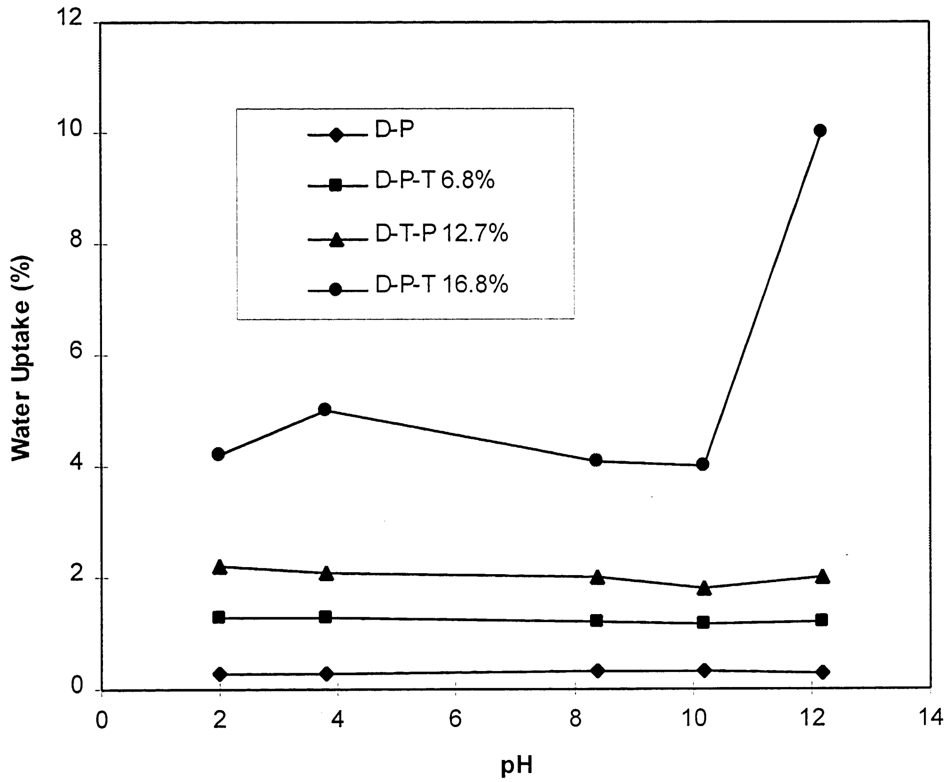


Figure 2. Water uptake percentage of D-P and D-P-T with different content of L-tyrosine *versus* pH at 70°C for 24 hours.

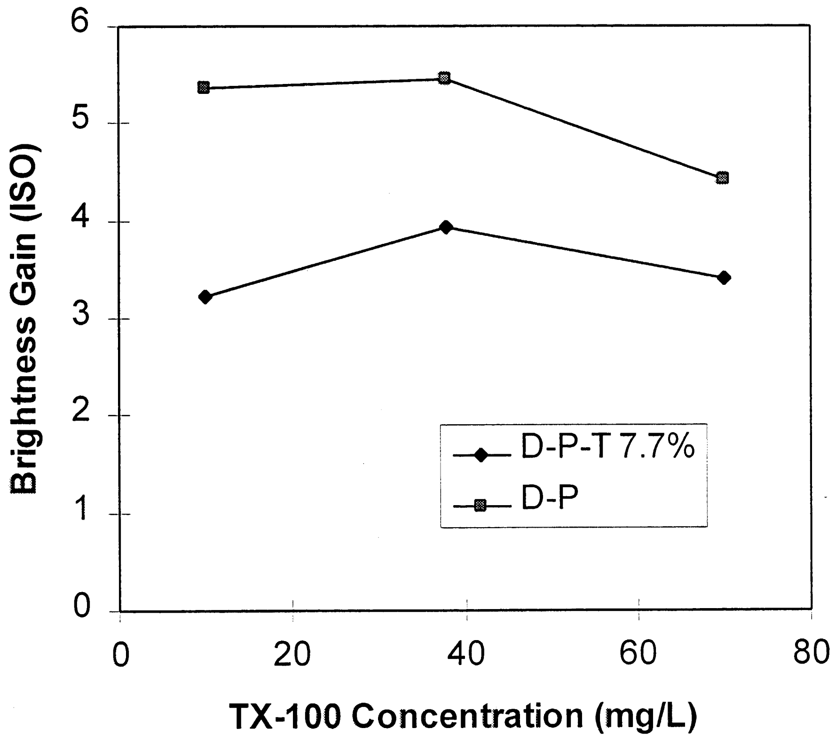


Figure 3. Brightness of handsheets made by flotation deinked pulps as a function of surfactant concentration.